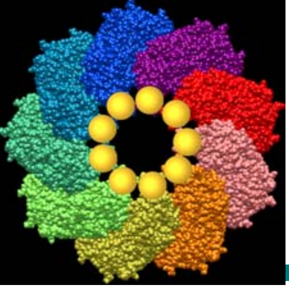


Manufacturing with Nanoparticles

Dr. M.C. Roco

Chair, Subcommittee on Nanoscale Science , Engineering and Technology, U.S. National Science and Technology Council

Senior Advisor, NSF, www.nano.gov and www.nsf.gov/nano

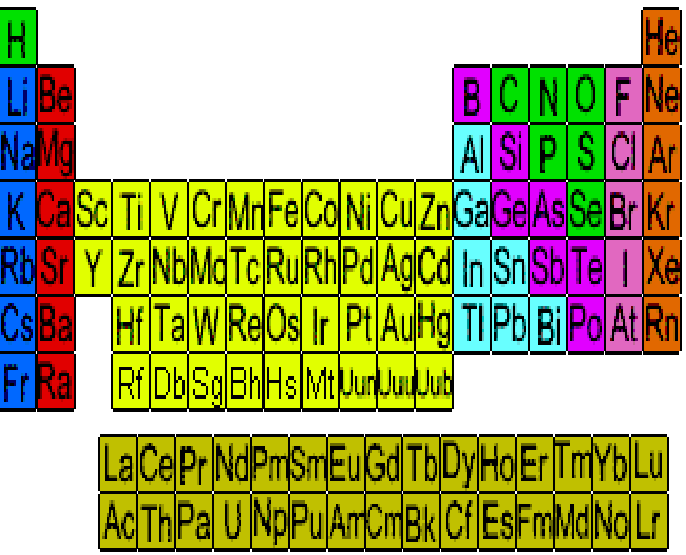
- **Functional nanoparticles and devices**
- **Four generations of nanomanufacturing**
- **The National Nanotechnology Initiative**
- **International perspective**

PARTEC Conference, Nuremberg, March 16, 2004

Manufacturing at the Nanoscale

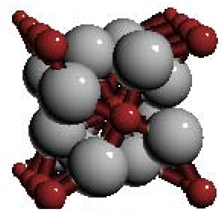
Transforming raw materials into products with desired properties and performance – generally in large quantities

Available atoms → structures "by design" → functional devices

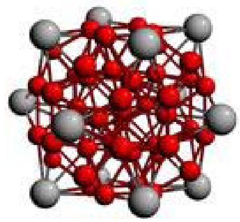


(NRL Center for Computational Materials Science)

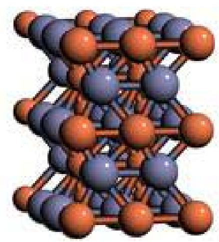
Al_2Cu



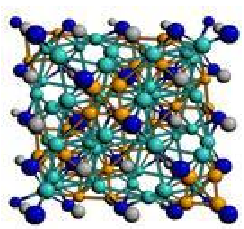
$BaHg_{11}$



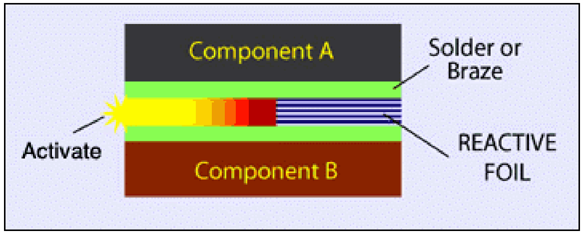
$MoPt_2$



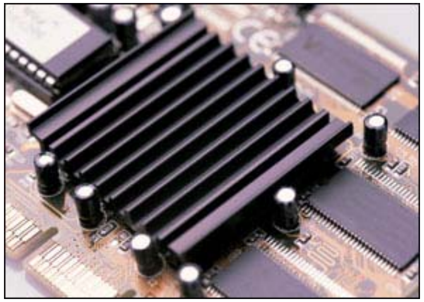
Fe_3W_3C



~ 5,000, 10 –20 nm alternating layers of Ni - Al



Reactive Nanotechnologies



Highly localized, low-energy, high-T, heat source

Atoms, molecules → 'nanoparticles' → materials/devices/systems

Utilization of Nanoparticles

- Introduction -

- **Nanoparticles (NP) may play two roles**
  - precursors for functional structures, devices and systems
  - agents of change (enhancing or changing) of physical phenomena, chemical and biological processes
- **NP take advantage of**
  - new physical/chemical/biological properties because of the size/shape
  - new molecular structures and architectures by nanofabrication, chemistry and biotechnology routes
- Few NP synthesis processes were developed decades ago. Currently, NP are commercially available (particle polymerization started during the second WW; self-assembly of micelles; synthesis of colorants), and one-dimensional nanostructures are used for GMR, supperlatices, coatings as optical and thermal barriers, hard coatings
- Present challenge: control, use various materials, processing, 3D structures, bottom-up methods, scale-up

Manufacturing at Nanoscale
- challenges -

- Create tailored structures in the 0.1-100 nm range
- Combine top-down and bottom-up approaches
- Integration along scales with larger systems
- Large scale production and economical scale up: different concepts and principles?
- *Interaction non-living and living structures*
- *Replication (ex: lithography)*
  Self-replication (ex: bio, DNA-based)
- *Revolutionary processes envisioned*
  Extend existing manufacturing capabilities if possible

Manufacturing at Nanoscale
- typical bottom-up processes -

- Nucleation and growth
  - Aerosol and colloidal dispersions; deposition on surfaces
- Selfassembling
  - Natural process in living systems and biomimetics
  - Chemistry/chemical manufacturing
  - Guided by electric, magnetic, optical fields
  - DNA controlled
- Templating
  - Al and carbon nanotubes; Substrate patterning
- Engineered molecules and molecular assemblies

  (a) Designed molecules as devices
  (b) Wires, switches, logic components;
  (b) New molecular architectures by design
- Bio methods: (a) Selectivity; (b) Assembling

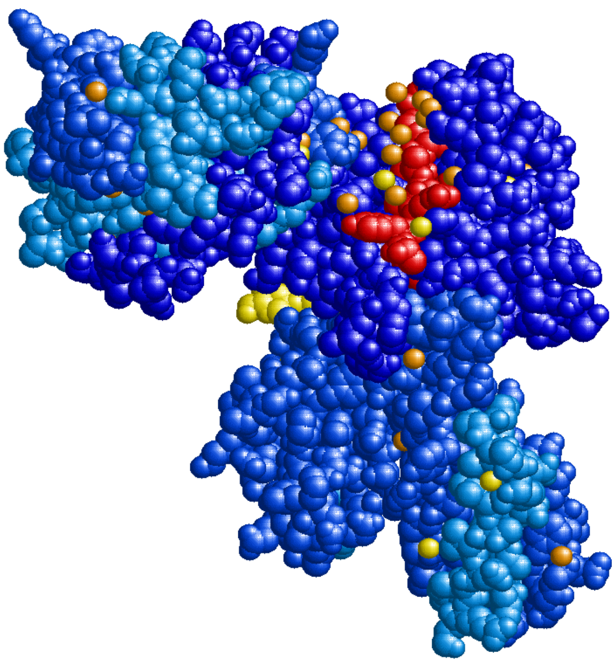
Manufacturing at Nanoscale
- other typical processes -

- Lithography:
  - Optical, ultraviolet, electron-beam (1-10 nm)
  - Scanning probe microscope based (1-10 nm)
- Nano-machining
- Nano-manipulation
  - Atoms and molecules (IBM), nanoparticles (USC)
  - 1D, 2D and 3D structures; assembling of nanodevices
- Fragmentation: mechanical milling, spark erosion, etc.
- Sintering of nano precursors
- Thermal treatment of metals, ceramics, composites
- Mixing of nanocomposites and their processing

Selfassembling: The Model of Molecular Biology

DNA $\xrightarrow{\text{Transcription}}$ RNA $\xrightarrow{\text{Translation}}$ polypeptide $\xrightarrow{\text{Folding}}$ functional protein

Linear nucleic acid	Linear nucleic acid	Linear amino acid sequence	Three-dimensional structure



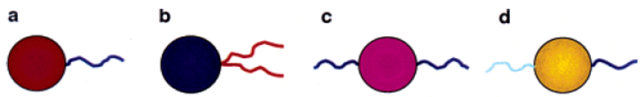
•All information leading to final folded structure is contained with the gene sequence

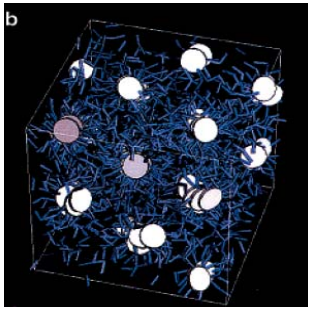
•Protein polymers spontaneously fold to final 3-D structure (U. Penn.)

Directed selfassembling

Ex: Approach based on surface recognition (Harvard U.)

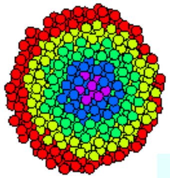
H.O. Jacobs, A. R. Tao, A.Schwartz, D. H. Gracias, G. M. Whitesides



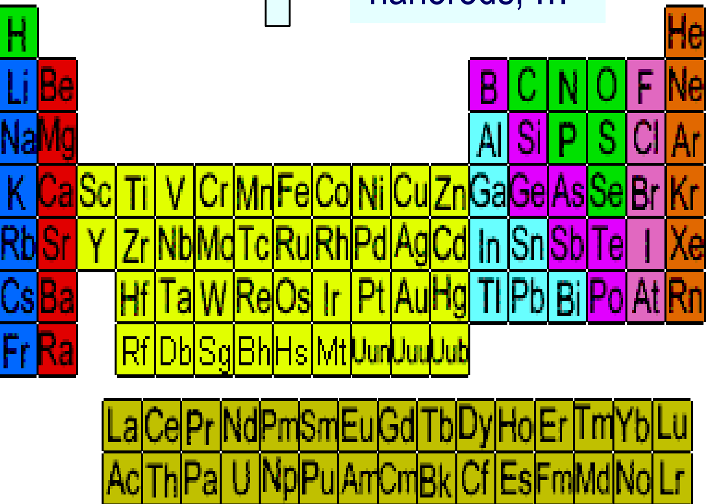


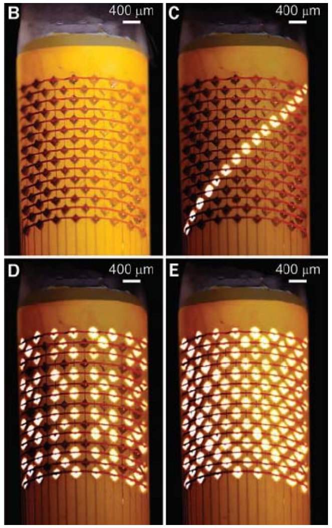
Attach oligomeric, polymeric, or biomolecular tethers

Directed self-assembly of building blocks



Form nanospheres, nanorods, …





Increasing scale of selfassembly of building blocks directed by:

- Electric fields
- Structured light
- Patterned substrates
- Free-energy minimization

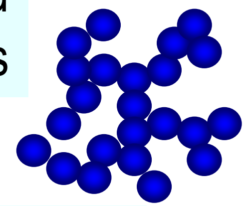
Goal: scaffolds, structures for

- **Catalysis**
- **Hydrogen storage**
- **Fuel cells**
- **Tissue engineering**
- **Drug delivery**
- **Electronics**

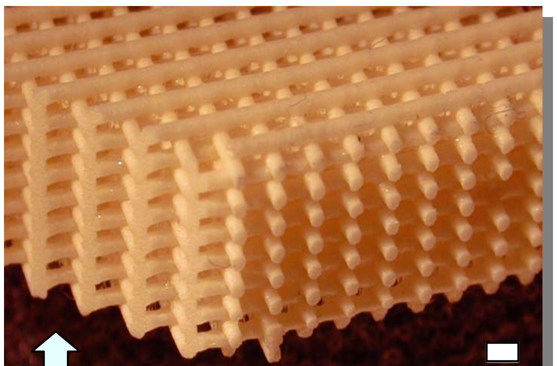
Directed selfassembling

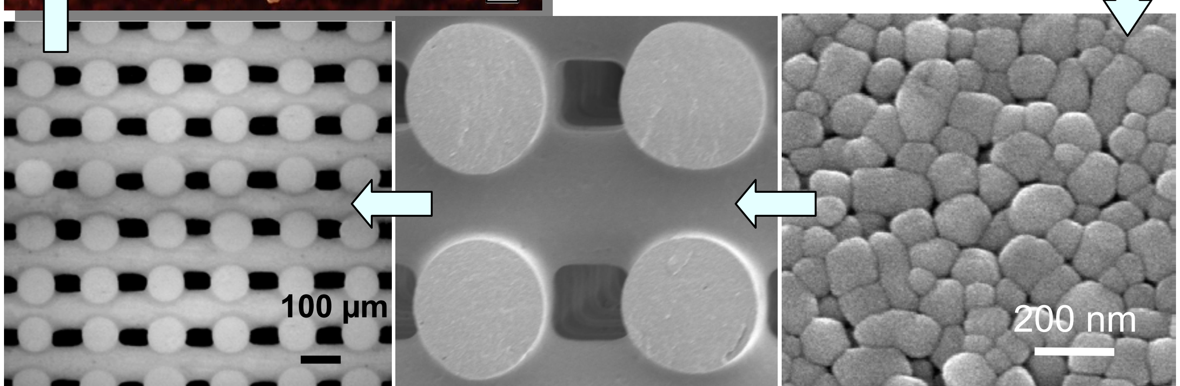
Ex: Robotic deposition of nanoparticle/polymer gels

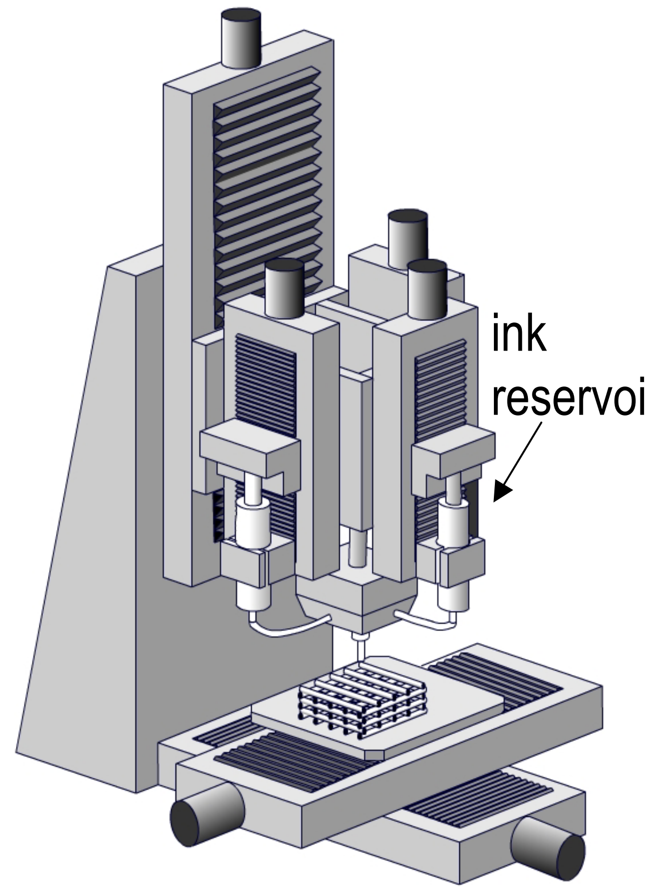
nanostructured
inks



direct-write assembly
of 3-D structures with
builds rates ca 1 mm/s
D nozzle: 1μm -1mm
Lewis et al. (2003)







Goal: Design nanostructured inks with controlled rheology and create materials with 3-D features on multiple length scales (RPI)

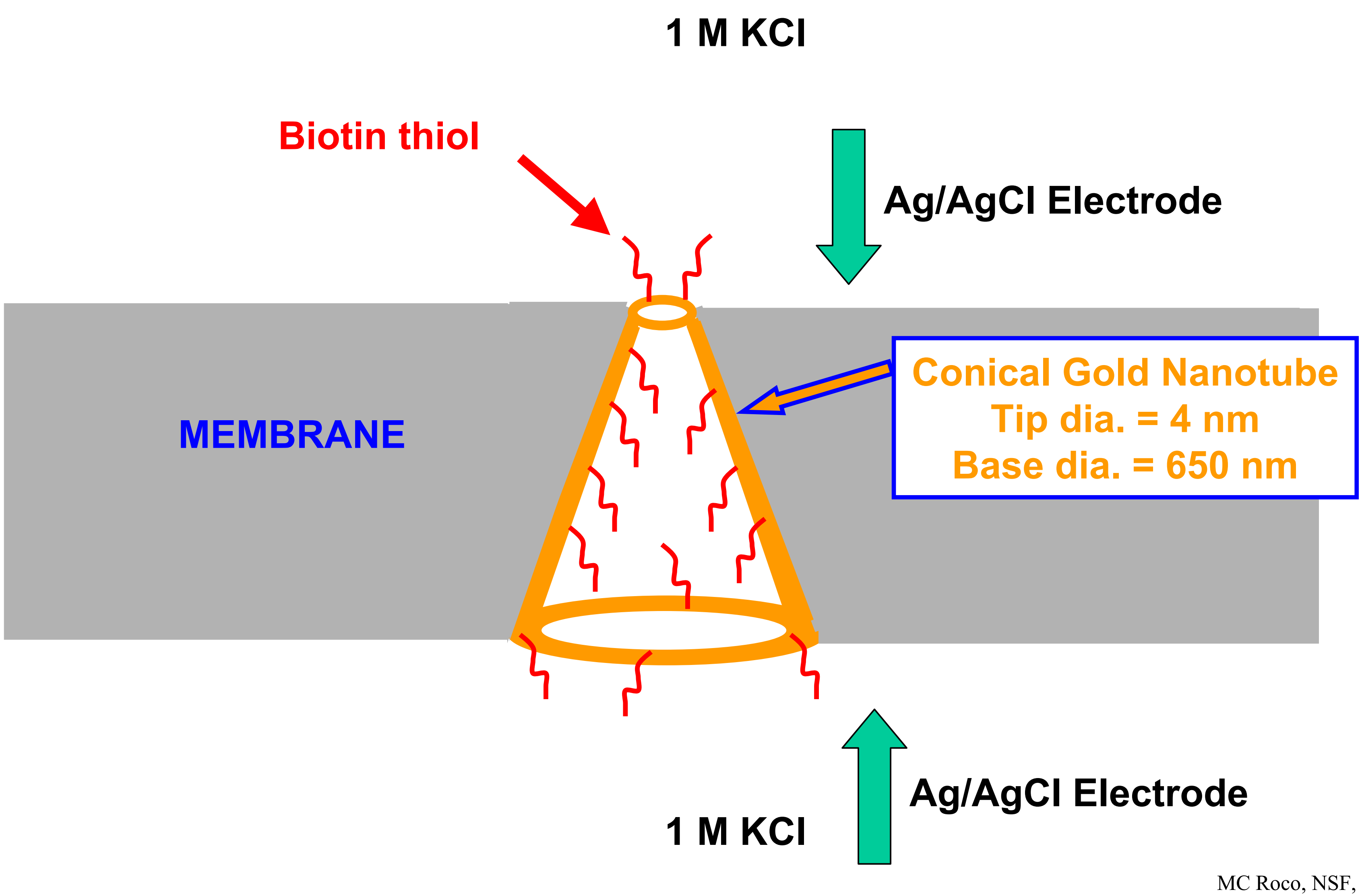
Templating nanomaterials

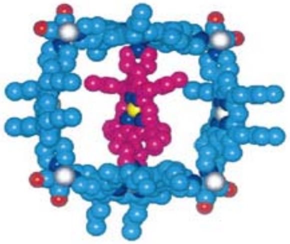
Nearly any synthetic method used to prepare bulk materials can be adapted:

the template used as a mechano-chemical reactor

- Electrochemical metal deposition.
- Electroless metal deposition.
- Electrochemical polymerization.
- Chemical polymerization.
- Chemical vapor deposition.
- Sol-gel methods.
- Hydro-thermal methods

Ex: A gold nanotube with a small tip d = 4 nm for a streptavidin sensor (Martin et al., U. Florida)





Timeline for beginning of industrial prototyping and commercialization

Accidental nanotechnology: since **1000s yr** (carbon black)

Isolated applications (catalysts, composites, others) since **1990**

Four generations of nanomanufacturing:

- **First Generation: passive nanostructures**
  in coatings, nanoparticles, bulk materials (nanostructured metals, polymers, ceramics):
  ~ 2001 –
- **Second Generation: active nanostructures**
  such as transistors, amplifiers, targeted drugs and chemicals, actuators, adaptive structures:
  ~ 2005 –
- **Third Generation: 3D nanosystems**
  with heterogeneous nanocomponents; complex networking and new architectures
  ~ 2010 –
- **Fourth Generation: molecular nanosystems**
  with heterogeneous molecules, based on biomimetics and new designs
  ~ 2020 (?) -

M.C. Roco, AIChE Journal, 2004

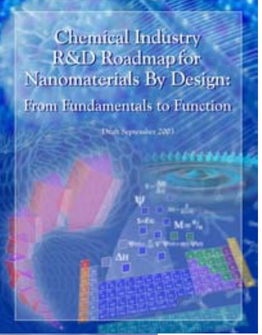
First generation of products: passive nanostructures (~ 2001 –)

- IN PRODUCTION -

- **Goal: Reaching systematic control in passive nanoscale domains, typically for tailoring macroscale properties and functions**

- **Ex. applications:** coatings, nanoparticles, dispersions, nanolayers, sintering, filters, surface nanopatterning, bulk materials - nanostructured metals, polymers, ceramics. Areas of relevance are:
  - Materials
  - Chemicals, including catalysts
  - Pharmaceuticals
  - Electronics

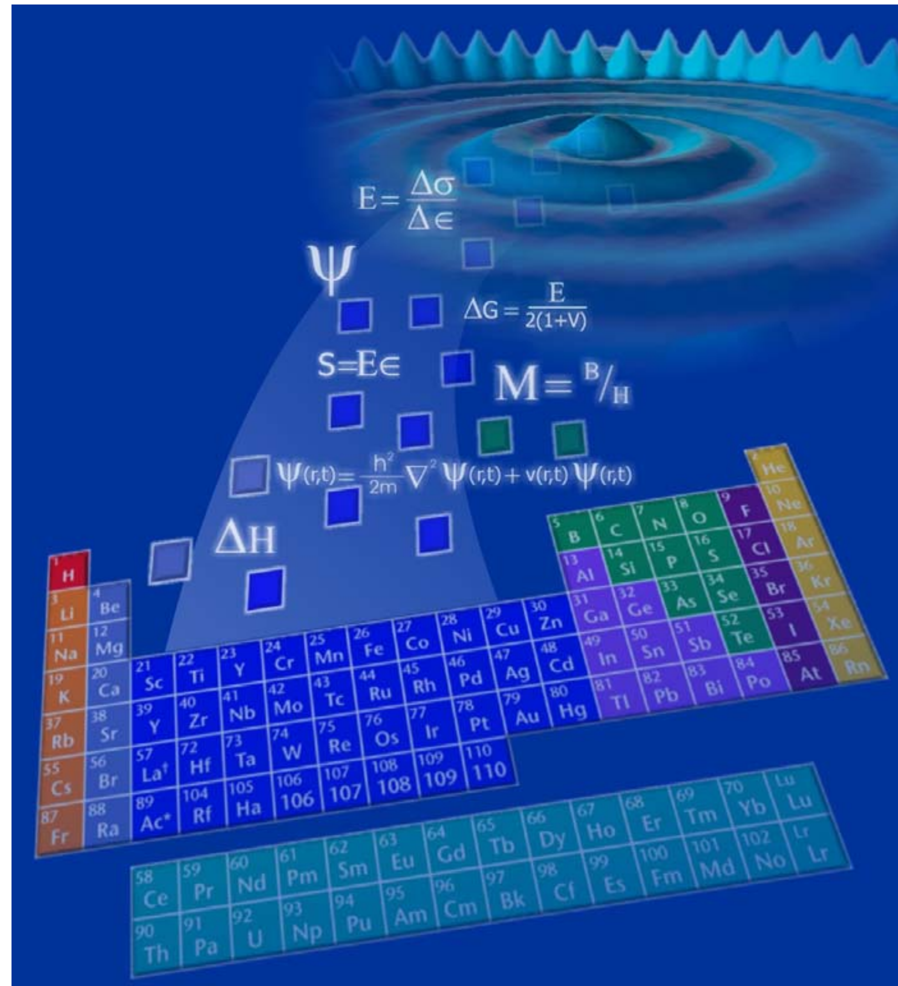
- **R&D focus: on nanostructured materials and tools Ex.: grain boundary simulation, nanomechanics**



Nanomaterials By Design

www.ChemicalVision2020.org and NNI

The ability to employ scientific principles in deliberately creating structures with nano-scale features (e.g., size, architecture)
that deliver unique functionality and utility for target applications



Nanomaterial Development: Future

Application-based Problem Solving

Start with existing needs, problems, or challenges in end-uses

→

Design, produce, and scale up nano-based materials with the exact properties needed*

→

Large numbers of diverse products based on nanomaterials "By Design" rapidly enter and succeed in multiple markets

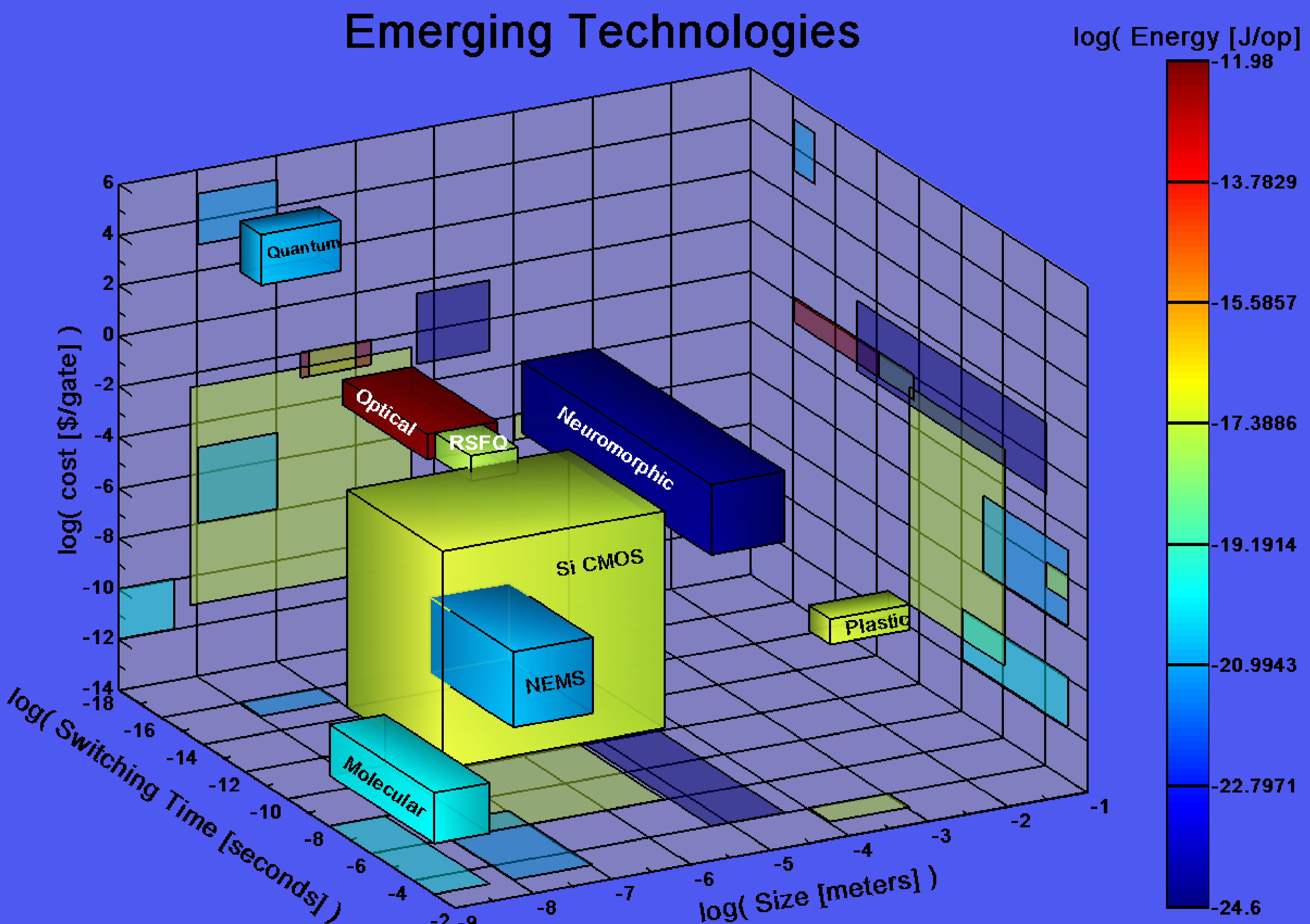
* Based on established understanding and methods

Second generation of products: active nanostructures (~ 2005 –)
- IN DESIGN -

- **Goal**: active nanostructures for mechanical, electronic, magnetic, photonic, biological and other effects, typically for microscale devices and systems

- **Ex. applications**: Targeted drugs, actuators, transistors, sensors, molecular machines, light-driven molecular motors, plasmonics, nanoscale fluidics, various devices. Emmerging areas are:
  - Nanomedicine
  - Energy conversion and storage
  - Agriculture and food systems
  - Realistic multiphenomena/multiscale simulations
  - Environmental applications

- **R&D focus**: novel devices and device system architectures



Motivation for hybridizing other devices with CMOS

Third generation of products: 3D nanosystems (~ 2010 –)

- IN RESEARCH -

- Goal: engineer and manufacture three-dimensional heterogeneous nanosystems, typically for nanoscale components
- Ex. applications: multiscale selfassembling, networking of structures and devices at the nanoscale with new architectures, nanosystems with long scale order, biomedical. Emerging areas are:
  - Nanosystem biology for medicine
  - Nanosystem architectures
  - Realistic multiphenomena/multiscale simulations
  - Environmental bio implications
  - Converging new technologies from the nanoscale
- R&D focus: Design and interaction of supramolecular systems and heterogeneous nanostructures

Fourth generation of products: molecular nanosystems (~2020?)

- IN RESEARCH -

- Goal: heterogeneous molecular nanosystems, typically for nanoscale systems and hybrid bio-assemblies

- Ex. applications: molecules as devices, monitor and condition cells as nanobiosystems, multiscale selfassembled systems, high added value ‘smart’ or/and adaptive components in larger systems

- R&D focus: atomic/molecular design, collective behavior and chemical-mechanical interaction of molecules, nano-bio-info-cognitive convergence, neuromorphic enginering

Several key issues

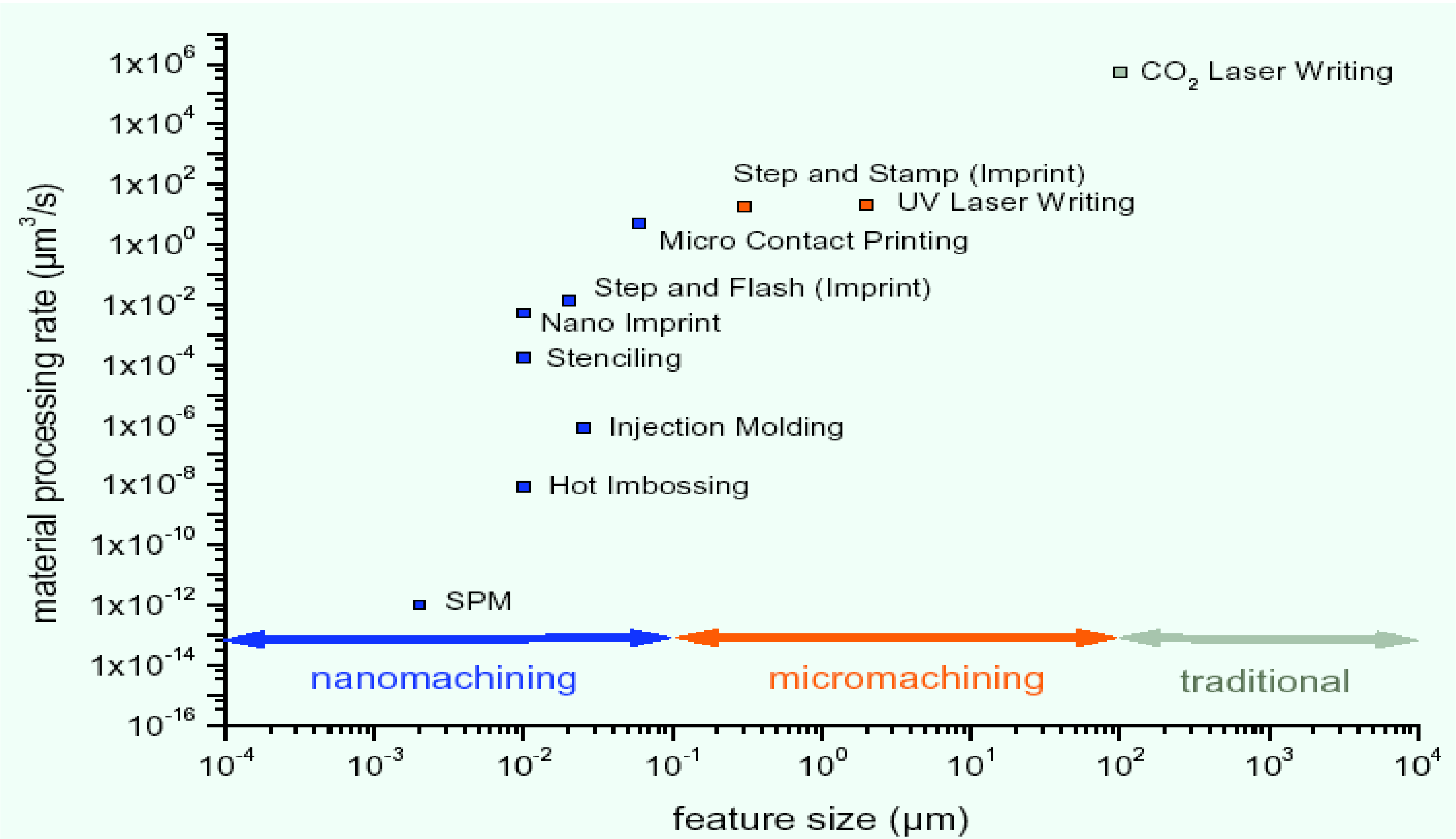
- Specific nanotechnology processes and equipment; expand on existing infrastructure
- Need for instrumentation and metrology
- Integrating length scales in 3-D, time scales, materials, functionality (mechanical, electromagnetic, thermal, biological, chemical) of manufacturing processes from macro to micro to nano
- Scaling up / high rate production requirements
- EHS requirements and research needs

Several key issues
a. Nanotechnology processes and equipment

1. **Conventional micro and nano fabrication**
   - Electron beam lithography
   - Photolithography
   - Thin film etching and deposition
   - Oxide and semiconductor thin film growth
2. **Synthesis, nanostructured coatings, & molecular assembly**
   - Nanotube and nanowire growth
   - Self-assembly
   - Cell culture/biological coatings/templates
   - Nanoparticle synthesis and characterization
   - Porous materials
   - Nanocomposites
   - Molecular synthesis
   - Electrophoretic particle deposition
3. **Novel patterning, structuring, manipulation & assembly**
   - Imprint Lithography/microcontact printing
   - Nanozerography
   - Interferometric lithography
   - SPM lithography/direct manipulation/Dip pen
   - Nanopore formation
   - Quantum dot growth/patterning
   - Optical tweezers
   - Chemically directed assembly of particles/devices
4. **Inspection and characterization**
   - Scanned probe characterization
   - Confocal microscopy
   - Ultrahigh resolution electron microscopy
   - Particle microscopies and spectroscopies
5. **Simulation, modeling, & visualization**

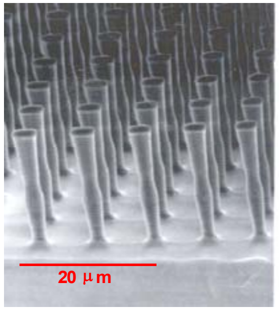
Scaling length and time scales of manufacturing processes from macro to micro to nano.

(Courtesy: A. Menon, Technical University of Denmark)

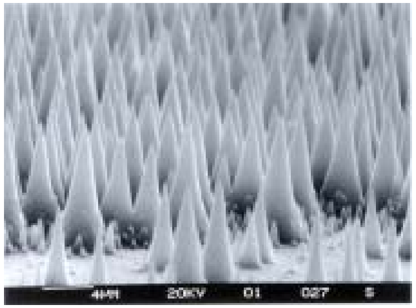


b. Nanomanufacturing: scaling up

- Focus on manufacturing **SCALE-UP** issues for industrial production: *producibility, predictability, productivity*

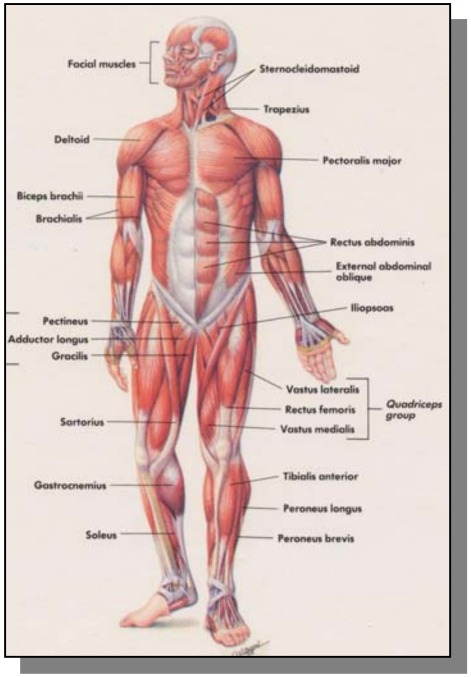


Micropost pattern

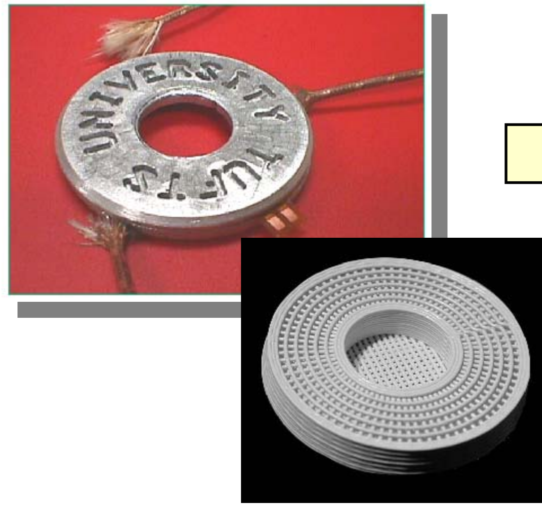


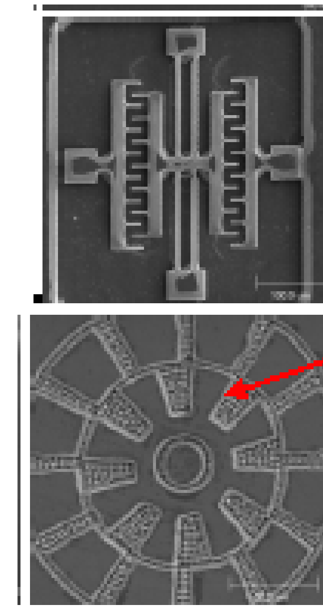
Nanopost pattern

- Emphasis on 3-D systems **UP-SCALING**
  - integration across dimensional scales: *nano-structures → functional devices → system architectures → products & services*
  - integration of materials, geometries
  - integration of functionality *(mechanical, electromagnetic, thermal, biological, chemical)*

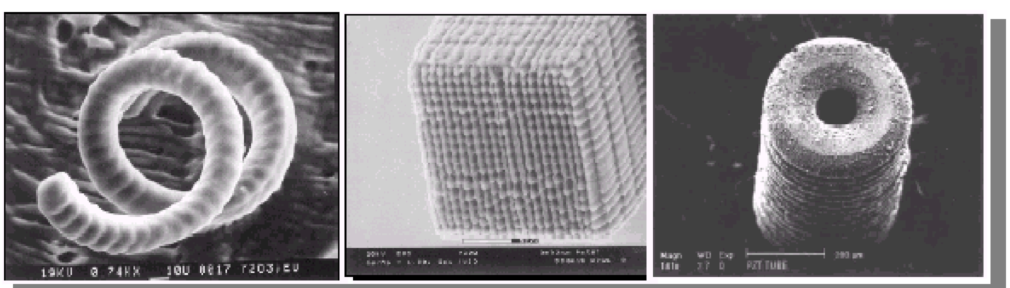


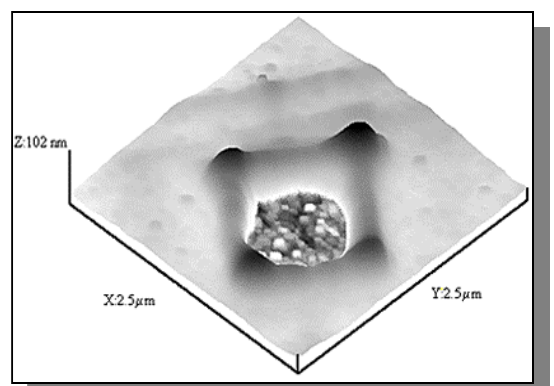
Manufacturing and Materials Processing and Integration Across Scales (UCLA)





Macro→ Meso→ Micro→ Nano





C. Nanotech EHS Questions and R/D Needs

- Toxicology of new chemicals and materials considered for use in microelectronics and nanotechnology areas
- Interaction of nano-particles with biological systems
- Validation of the current standard methods for EHS assessment of materials
- Development of new methods for rapid and reliable assessment of the EHS impact of process chemicals and product materials.

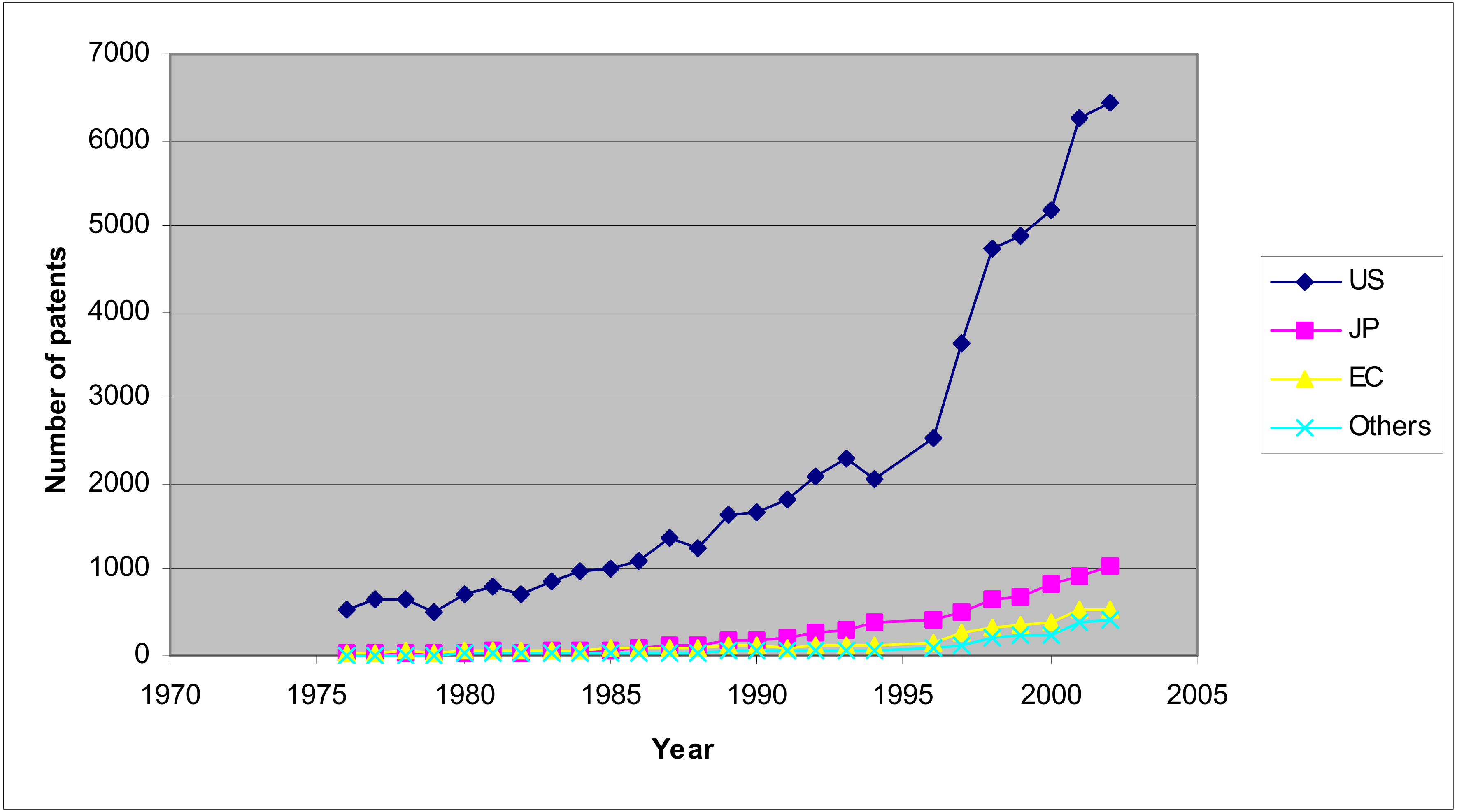
Nanotech EHS Evaluation

For: Raw materials/ Manufacturing & tools (metrology)/ New process byproducts / Product contents

For: Particles, surfaces

d. Nanotechnology patents per region (NSF, 2003)

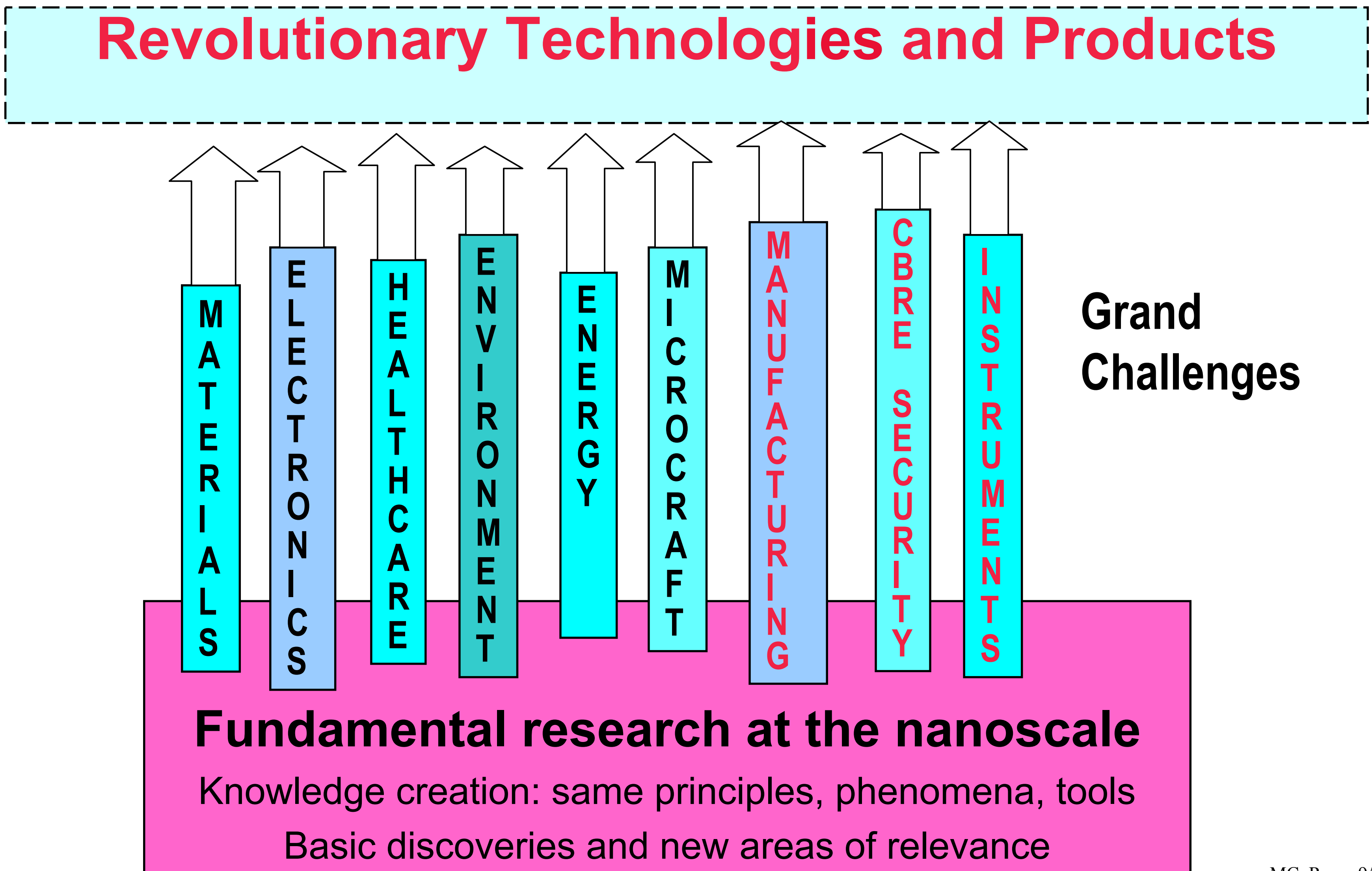
Searched by keywords at USPTO : nano*, atomic force microscop*, atomistic/molecular simulation, biomotor, molecular device, molecular electronics, molecular modeling, molecular motor, molecular sensor, quantum computing, quantum dot*, quantum effect*, scanning tunneling microscop*, selfassembl*



www.nsf.gov/nano (from J. of Nanoparticle Research, 2003)

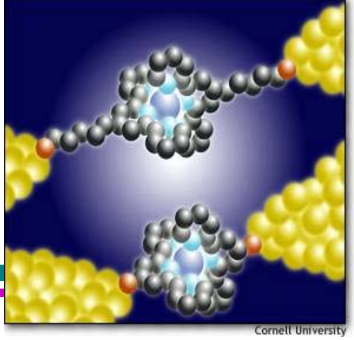
National Nanotechnology Initiative (16 agencies, R&D $1B/year)

Interdisciplinary "horizontal" knowledge creation, versus
"vertical" transition from basic concepts to Grand Challenges



NNI: Nanotechnology

Definition on www.nano.gov/omb_nifty50.htm (2000)



- **Working at the atomic, molecular and supramolecular levels, in the length scale of approximately 1 – 100 nm range, in order to understand, create and use materials, devices and systems with fundamentally new properties and functions because of their small structure**

- **NNI definition encourages new contributions that were not possible before.**

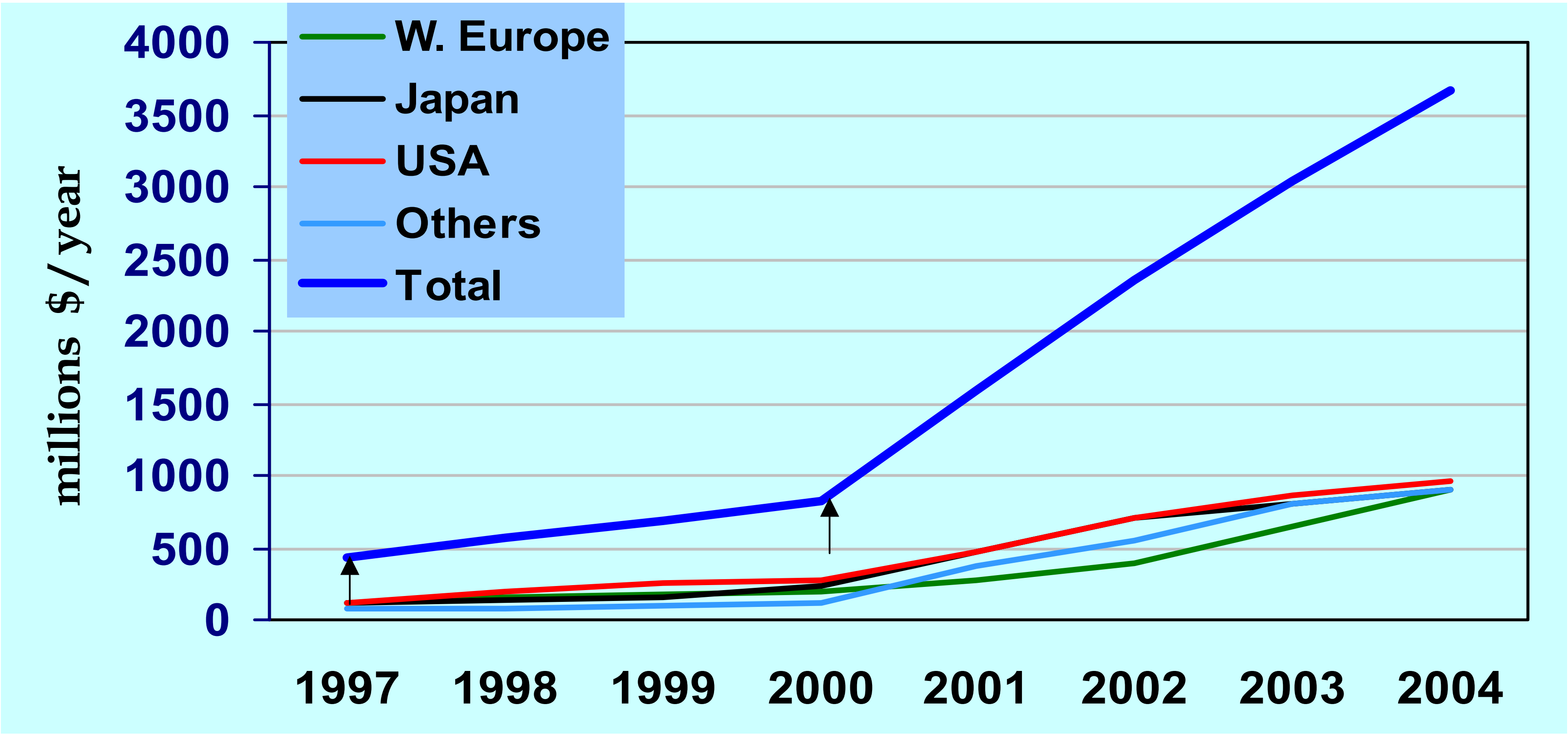
  - novel phenomena, properties and functions at nanoscale, which are nonscalable outside of the nm domain

  - the ability to measure / control / manipulate matter at the nanoscale in order to change those properties and functions

  - integration along length scales, and fields of application

Context – Nanotechnology in the World

Government investments 1997-2004 (estimation NSF)



Note:

- U.S. begins FY in October, six months in advance of EU & Japan (in March/April)

“Nanoparticle Synthesis and Processing” program
NSF, 1990 - ($3 million)

<u>GOAL:</u> SYNTHESIS & PROCESSING OF NANOPARTICLES

<u>NICHE</u>: PRODUCTION AT HIGH RATES; SPECIAL PROPERTIES

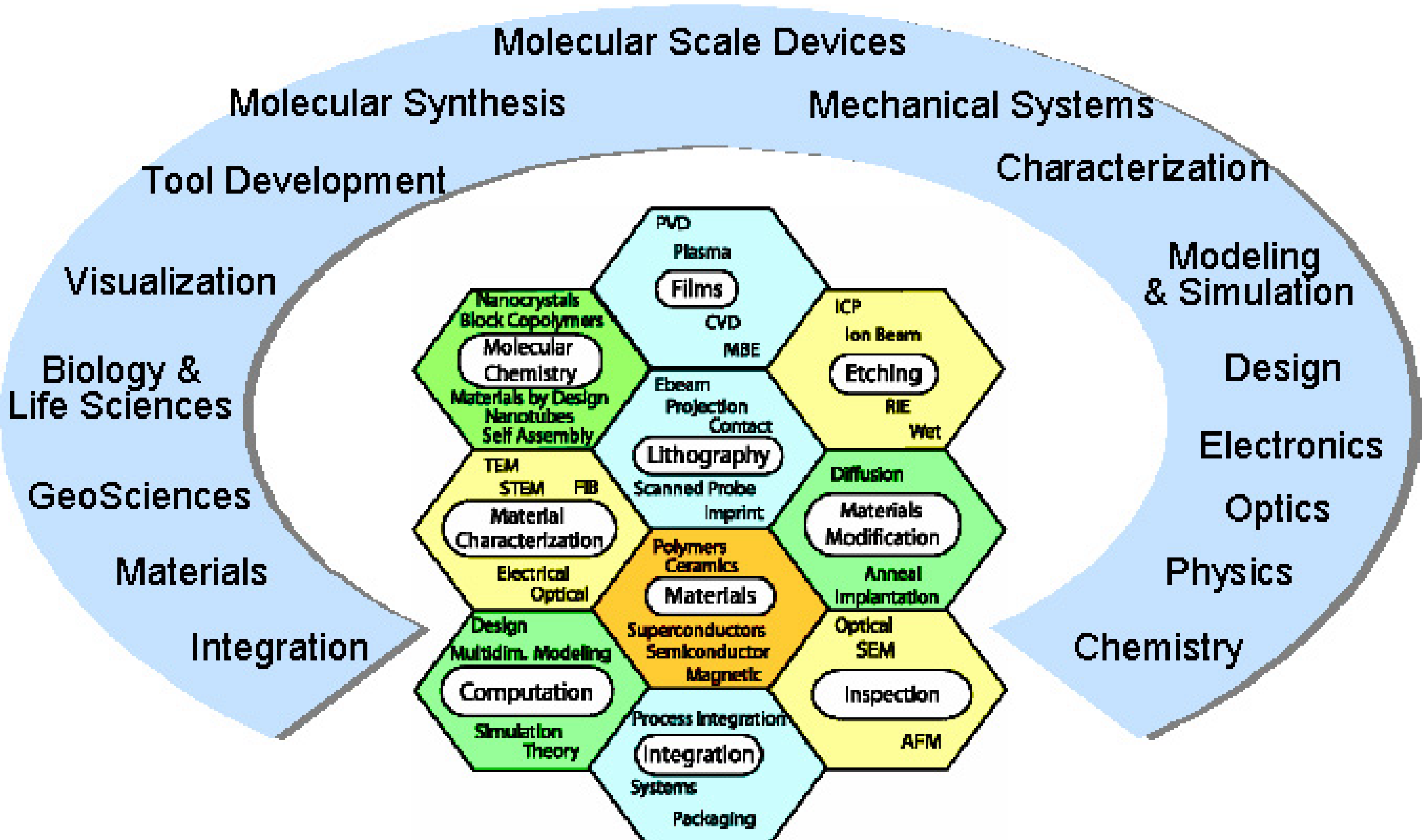
A PROJECT HAS CO-P.I. FROM DIFFERENT DISCIPLINES. Ex.:

- *Nanoparticle Formation Using a Plasma Expansion Process, U. MN*
- *Nanocrystalline Materials Prepared by Spark Erosion, UCSB*
- *Controlled Production of Nanoparticles Using Microemulsions, MIT*
- *Combustion Process for Nanosized Reinforced Composites, U. WA-SL*
- *High Volume Production Using Laser Ablation of Microparticles, UT*
- *Particle-particle and Particle-substrate Interactions, Purdue U.*
- Others*: Submicron Aerosol Agglomeration, UCLA*
- *Nanophase Composite Materials for Magnetic Refrigeration, SUNY-B*
- *Effect of Electric Fields in Nanoparticle Flame Reactors, U. Cincinnati*

NNI and nanomanufacturing 2000-

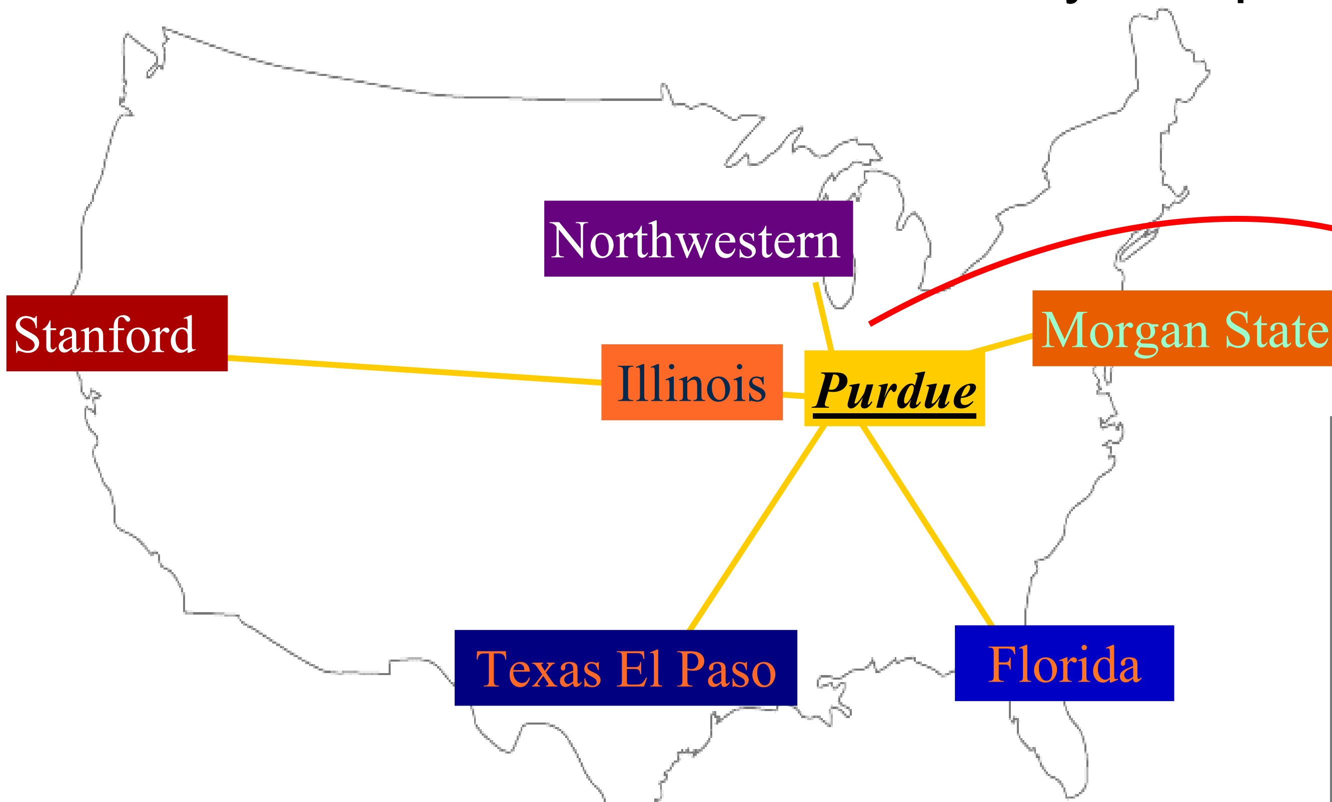
- Initial goal; a key reason for NNI
- A new Grand Challenge in 2002
- About 1/3 NNI budget has relevance to NM crossing other fields; to continue for all four generations of nanomanufacturing
- Evaluations: NRC (Academies), PCAST, OMB/OSTP

NSF National Nanotechnology Infrastructure Network (13 nodes)



Network for Computational Nanotechnology (7 nodes)

Multi-scale, multi-disciplinary from "atoms to systems" research, education, user-facility components



~ 2500 users worldwide
www.ncn.purdue.edu

www.nanohub.purdue.edu

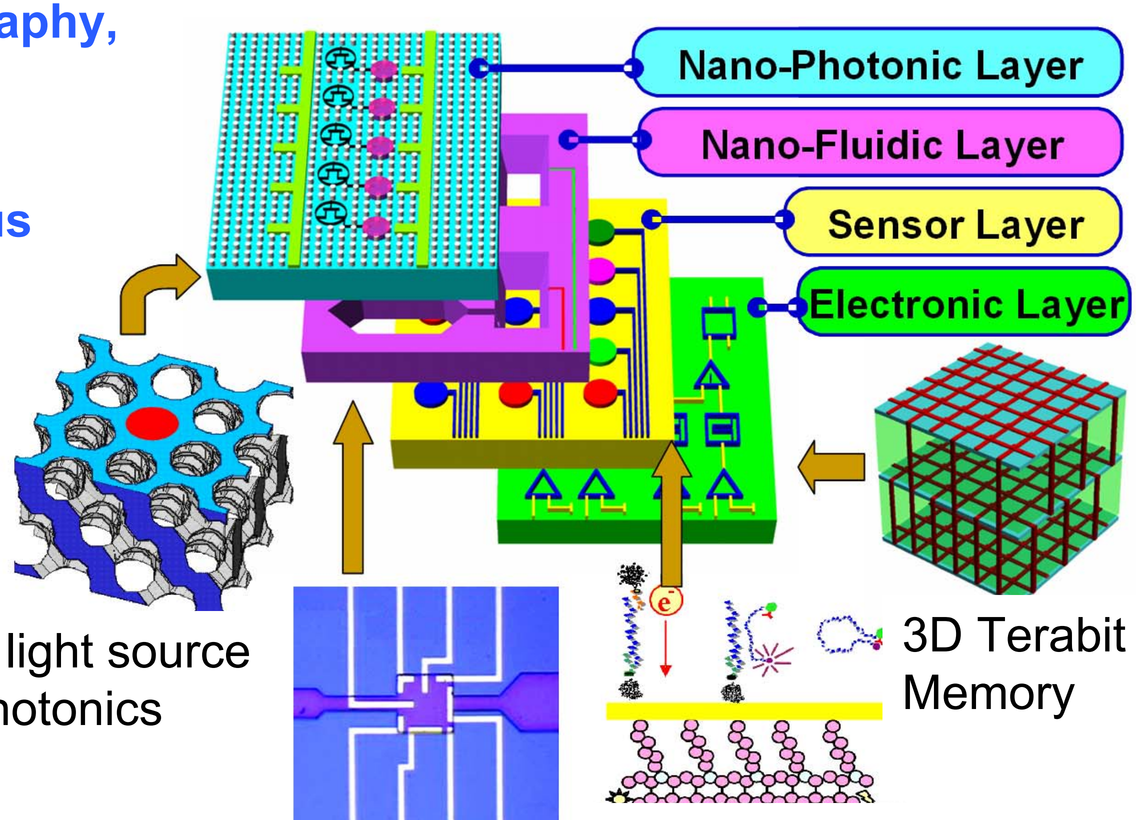
Center of Scalable and Integrated Nanomanufacturing

UCLA, UC Berkeley, Stanford U., UCSD, UNCC, HP Labs

Goals

- 3D nano-manufacturing with 1-20 nm resolution (Plasmonic Imaging Lithography, Ultra Mold Imprinting)
- Massive and parallel integration of heterogeneous nano-LEGOs into devices
- Nano-manufacturing cluster tool

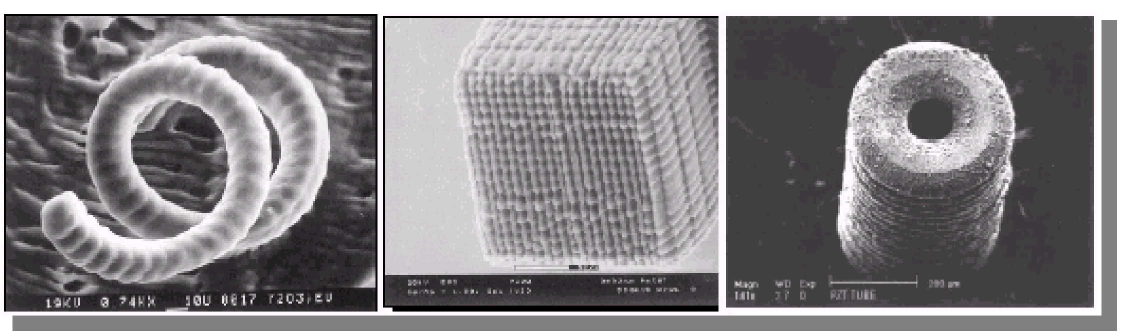
Research Thrusts



Center for Scalable and Integrated Nano-Manufacturing

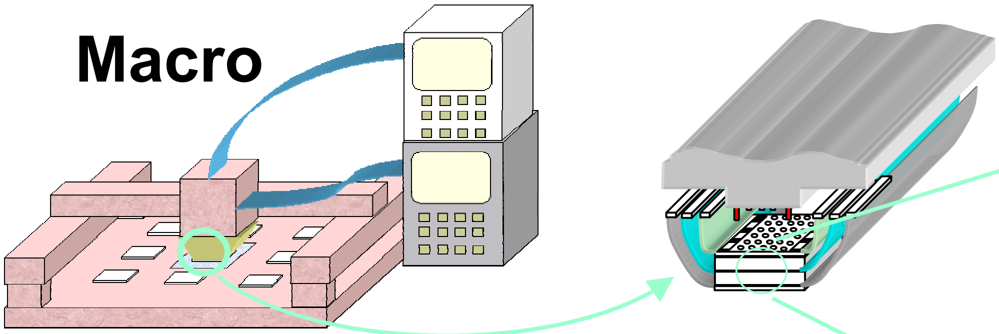
UCLA, UC-Berkeley, Stanford, UC-San Diego, UNC-Charlotte *(~$18M, 5 years)*

- **plasmonic imaging lithography, nano-imprinting, ultra-molding and imprinting lithography (sub-20nm 3D nano-manufacturing)**
- **field-assisted parallel nano-assembly (massively parallel integration)**
- **nano-scale precision engineering/tooling/metrology, nano-CAD platform, cluster tool**
- **nanoelectronics/nanophotonics/biosensor testbeds**
- **workforce development – LA school district, CA science center**

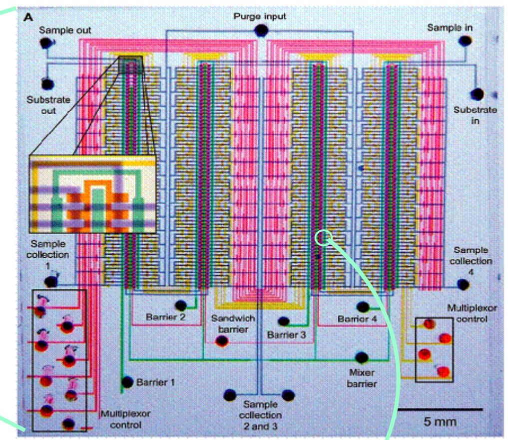


Nanoscale Chemical-Electrical-Mechanical Manufacturing Systems, UIUC, NCSU, Caltech

Macro



Micro



Goals - control of composition at nanoscale

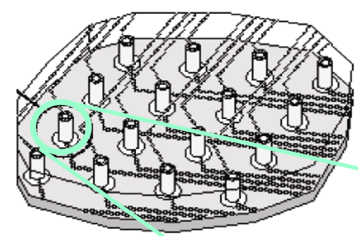
- placement of nanostructures in 3D
- knowledge of the state of matter at nano

Research Thrusts

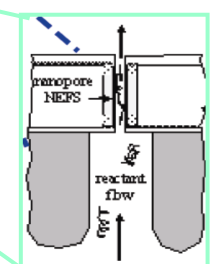
Micro-Nano Fluidic Network Toolbit

Process Sensing and Control

Manufacturing Systems



Nano



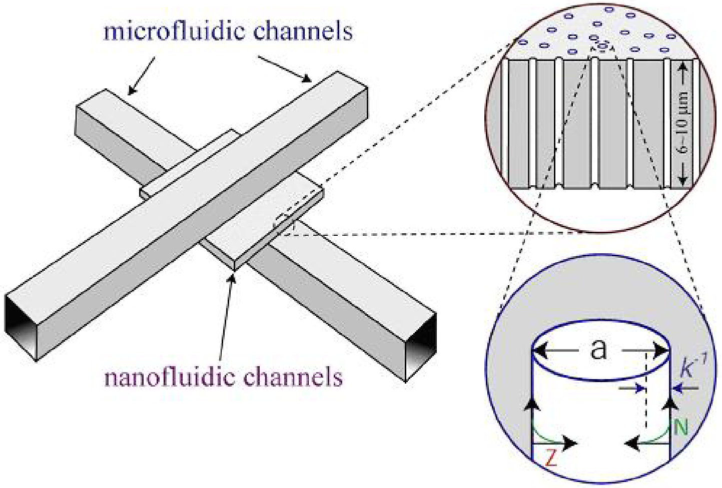
Nanoscale Chemical-Electrical-Mechanical Manufacturing Systems Center

U.Illinois (UIUC), North Carolina A&T, Caltech (~$13M over 5 years)

- molecular gate array tool, electronically controlled nanopores
- efficient electrokinetic flows, micro- and nano-fluidic networks
- nanoscale positioning and sensing
- nanoscale organic optoelectronic/combinatorial chemistry and biology array testbeds
- workforce development

  collaboratory,

  community colleges,…



DOE Nanoscale Science Research Centers

Summer ‘03

Center For Nanophase Materials Sciences at ORNL

Spring ‘05

Center For Functional Nanomaterials at BNL

Spring ‘04

Molecular Foundry at LBNL

Spring ‘04

Center for Nanoscale Materials at Argonne

Center for Integrated Nanotechnologies